Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 69 (2015) 299 – 309

Energy Procedia

International Conference on Concentrating Solar Power and Chemical Energy Systems, SolarPACES 2014

Impact of solar selective coating ageing on energy cost

H. Cachafeiro[a]*; L. Fdez. de Arevalo[a]; R. Vinuesa[a]; J. Goikoetxea[b]; J. Barriga[b]

[a] *Aries Ingeniería y Sistemas S.A., Paseo de la Castellana 130, Madrid 28046, Spain.*
[b] *IK4-Tekniker, Iñaki Goenaga 5, Eibar 20600, Spain*

Abstract

In order to overcome the current energy challenges and to find new ways of producing clean energy, the solar sector is focused on improving its performance and defining the adequate technology for each application. Nowadays the concentrated solar power (CSP) technology, which uses parabolic trough collectors, is the most mature and well-established concept. The technology is based on the concentration of solar radiation using parabolic reflective surfaces (typically glass mirrors) and focusing the collected energy on a receiver tube, which is placed on the geometrical focus of the parabola.

Solar selective coatings are applied on the surface of the receiver tube surface to improve its performance in stable conditions, but these nanocoatings suffer stresses during their operating lives, which reduce their optical properties and increase the cost of the produced energy. The development of selective coatings with improved optical properties is essential to the development of CSP technology. It requires improvements in the process of layer deposition, to enhance the characterization of the coating optical properties, and to monitor the coating status during the typical 25 years of operation.

In this study it has been analyzed the impact of the ageing of selective coating in the energy gain and thermal losses and, as a consequence, the necessary evolution of CSP technology to reduce the cost of energy.

Peer review by the scientific conference committee of SolarPACES 2014 under responsibility of PSE AG

Keywords: Absortance; Emittance; Reflectance; Selective coating; Ageing

* Corresponding author. Tel.: +34 915702737.
E-mail address: hcachafeiro@aries.com.es

1876-6102
Peer review by the scientific conference committee of SolarPACES 2014 under responsibility of PSE AG
doi:10.1016/j.egypro.2015.03.034

1. Introduction

Coatings for Parabolic Trough technology are applied on the surface of the internal metallic tube. These selective coatings are aimed at achieving a high solar absorptive rate in the visible and near-infrared spectrum (300-2500nm), while a low value of solar emittance to the environment in the IR spectrum (1-30 µm) is maintained. Fig. 1 shows the spectral reflectance of a typical solar selective coating, where the characteristic spectrum of solar radiation in the visible and near-infrared range is also shown, as well as the characteristic blackbody radiation distribution in the IR region for a body at the solar receptor working temperature. According to the relationship of the reflectance with the absortance and the emitance it can be inferred that an ideal solar selective coating should exhibit low reflectance (thus high absorbance) in the region where the solar spectrum contains more energy, and high reflectance (leading to low emittance) in the spectral range of highest blackbody radiation. Both requirements cannot be met simultaneously and a compromise solution must be sought. In the case of a coating for a working temperature of 600ºC both reference curves, the sun radiation AM 1.5 and the blackbody profile, lie closer from one another than in the case of 400ºC, so the interaction between emissivity and absortivity is even stronger.

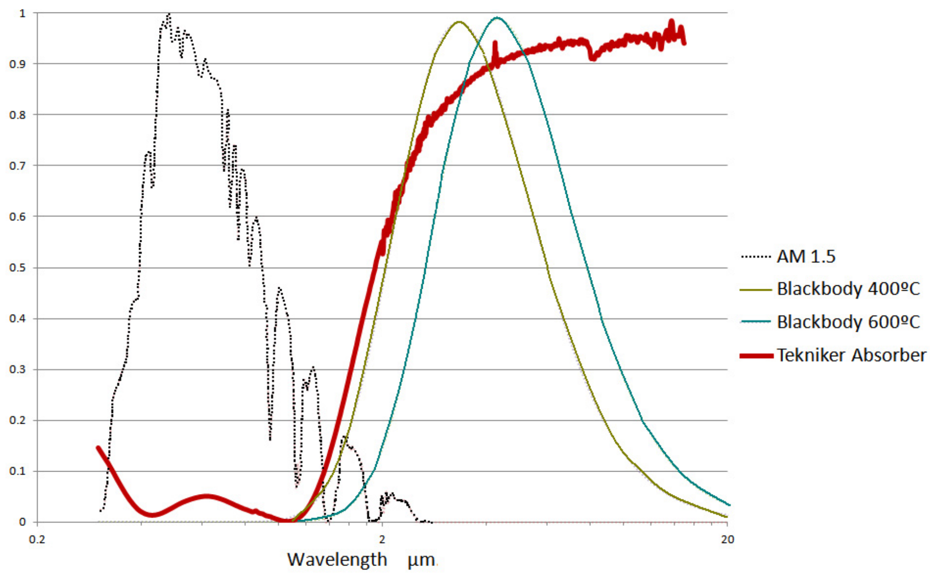

Fig. 1: Spectral reflectance of a typical solar selective coating

The coatings applied on the steel tube surface may suffer a modification of their optical properties because of the effect of working conditions in normal operation during their 25 years lifespan. Although there have been several attempts to develop testing protocols to assess these effects [1], a comprehensive procedure for the wide range of operation conditions has not been developed yet.

The ageing process mainly depends on the effect of temperature shocks, heating-cooling cycles and the presence of gases (such as oxygen and hydrogen) in the vacuum chamber where it is located (usually at pressure levels below 10^{-3} mbar). From an economical point of view, this effect results in a significant increase of the energy cost, as well as an uncertainty in the evolution of the future performance of a conventional solar plant.

2. Solar selective coatings

The stack that defines the selective coating is formed by several individual layers with different properties, providing the final required optical characteristics. The typical configuration of a solar coating is based on the combination of absorber and reflective layers, adding an antireflective layer on top in order to increase the ratio of effective solar rays, and an antidiffusion barrier between the substrate and the selective coating to protect the stack from migration of substrate elements.

2.1. Coating definition and its properties

The nanocoatings for solar applications are typically applied by sputtering or vacuum evaporation. Regarding the most typical materials and the deposition order, the most common configuration is the following: at the top, an antireflective layer made in SiO_2; for the solar absorbance several cermets are used: AlNx, MoOx, WOx, TiAlN, Mo, W, Ni, Co, Si, Ge in combination with transparent dielectrics: SiO_2, TiO_2, Al_2O_3); for the IR mirror a reflective layer (typically, Mo, Ag, Al) is chosen; and finally, in contact with the steel, an antidiffusion barrier made of Al_2O_3. The global performance depends on the nanometric properties of the stack, such as: thickness, crystallography, nanostructure, roughness and homogeneity. Typical optical parameters at operation temperatures of around 400ºC are 96% absorbance and 10% emittance [2], [3].

During the design of selective coatings one of the most powerful tools at hand is the possibility to tailor the optical characteristics of the cermets to the requirements of the coating. This is because by modifying the proportion of metal and dielectric in the cermet it is possible to obtain a wide range of different optical characteristics. As an example, Fig. 2 shows the variation on the n and k indices (indices of refraction and absorption), for different mixtures of Molybdenum in Si_3N_4. For the imaginary part, related to absorption, the indexes show variations between 0 and 1.5, covering all the attenuation degrees needed for this purpose.

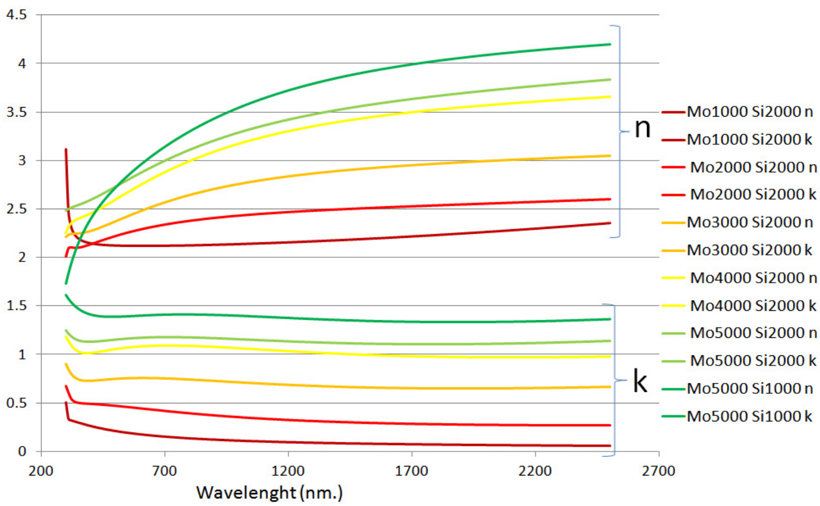

Fig. 2: Indices n and k for a number of different mixtures of Molybdenum in Si_3N_4.

The metallic content of the cermet is mainly in the form of small metallic islands of the order of 5 nm, dispersed in a dielectric matrix. For a certain proportion of metal in the dielectric (higher than those depicted in Fig. 2), those islands percolate. The size, shape and distribution of these islands depend critically on the details of the deposition process, so it is important to control the process in order to achieve good repeatability in the optical characteristics of the cermets.

2.2. Typical working conditions in a solar field

Solar selective coatings are applied on the steel tubes that are currently used in CSP technology. In order to set the basis of the operation conditions it is necessary to define two different working levels related to two different technical approaches.

The most common and well-known condition is called "medium temperature", and is defined by the combination of variables summarized in Table 1. Note that under this configuration, the thermal fluid flowing through the receiver tube is synthetic oil.

Table 1: Operational conditions in medium temperature

Working condition	Value
Maximum temperature of substrate	420 ºC
Maximum pressure in the chamber	1 bar
Minimum pressure in the chamber	10^{-3} mbar
Initial composition of chamber	100% Air
Final composition of chamber	Air + H_2

The alternative approach called "high temperature" regime is currently under investigation in terms of applicability and efficiency. An on-going project aimed at the development of a solar receiver designed to work at such high temperature conditions is HITECO [4]. The aim of this project is to increase the parabolic-trough efficiency, solving the current limitations of the technology. The operating conditions characteristic of this new concept, at high temperatures, are given in Table 2.

Table 2: Operational conditions in high temperature for HITECO concept

Working condition	Value
Maximum temperature of substrate	620 ºC
Maximum pressure in the chamber	1 bar
Minimum pressure in the chamber	10^{-3} mbar
Initial composition of chamber	Air + Kr
Final composition of chamber	Kr + Air + H_2

The innovations of the HITECO concept [1] are focused on: a) increase of the performance acting on the working temperature and geometrical approach, b) development of simpler and more reliable systems and c) decrease of the manufacturing cost by the vacuum of the chamber and acting on the entire mechanical design.

The receiver tube developed, and now under validation stage, integrates several innovative concepts in its design. Among them, the most relevant are:

- New geometrical approach, units of 12 m length rather than 4 m used in current designs.
- Total independence between the internal tube (steel) and external tube (glass).
- Dynamic vacuum in the interanular space; current concepts create the vacuum during the manufacturing process.
- Less severe working conditions, lower vacuum requirements.
- Flexible in operation and usable with any HTF.
- Continuous control of the state of the tube by monitoring its performance.
- Simplification of the manufacturing and assembling processes.

A significant goal of this project is to create an innovative selective coating capable of working in more restrictive conditions. This means that the coating has to withstand operation at 600ºC, instead of the typical maximum operating temperature of around 400ºC and with variable amount of oxygen in the vacuum chamber.

3. Ageing process

3.1. Ageing of coatings in solar tubes, causes and effects

When the selective coating has been under the operation conditions defined in Tables 1 and 2 the coating suffers a degradation process which affects its internal structure, thus modifying its optical values. This process has been assessed by means of the study case shown in Fig. 3, where five different layers are found: a 262 nm thick alumina antidiffusion coating, a silver coating of 181 nm, a high metal content cermet of 220 nm, a low metal content cermet layer of 78 nm and an antireflection layer of 86 nm.

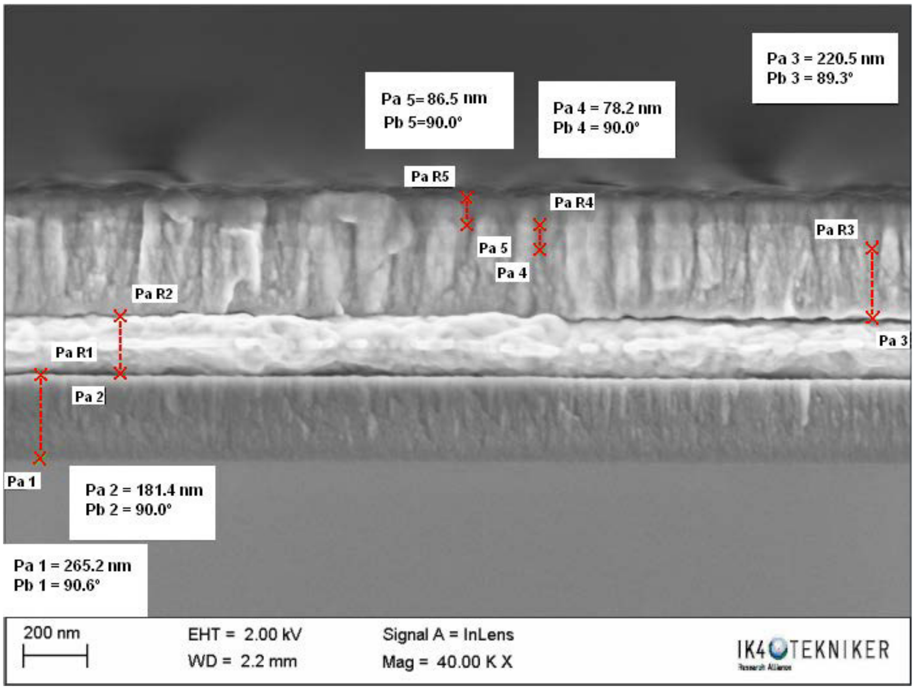

Fig. 3: Selective coating subjected to ageing analysis.

The alumina coating below the silver layer acts as a diffusion barrier to avoid the migration of atoms from the stainless steel substrate to the coating during its long working life (25 years) at 400ºC.

Fig. 4 shows the result of a Glow Discharge Optical Emission Spectrometry (GDOES) analysis on the surface of a stainless steel sample with a coating of alumina and Molybdenum on top, which was maintained at 700ºC in high vacuum conditions (10-4 mbar) for 64 hours to simulate the full lifetime migration on a working tube, according to the accelerated ageing criteria. These results show that none of the components of the steel could migrate past the alumina coating, although surprisingly some of the Molybdenum seems to have reached the steel substrate. This clearly shows that this kind of migration between layers is the main source of degradation of the absorber coating during its lifetime, and that it is often necessary to use diffusion barriers to avoid it. These barriers become more relevant as the working temperature increases.

Additionally, it was analyzed the evolution of the layers on a solar absorber with silver mirror which was subjected to 700ºC (considering an accelerating ageing process) during 12 hours in order to assess its endurance at working temperature. Fig. 5 shows a detailed visualization of the mirror in the selective coating, where each dark corresponds to a hole in the mirror layer generated as consequence of the self-arrangement of the silver atoms within its layer. The reflectivity is significantly deteriorated, and the emissivity of the absorber tube increased accordingly.

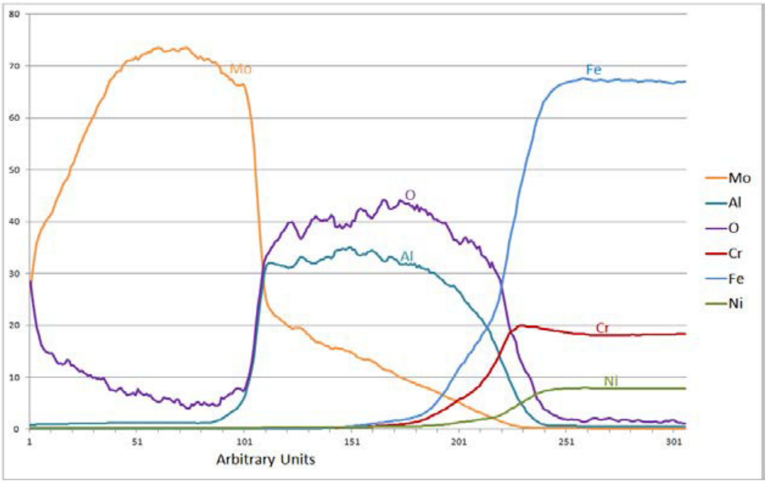

Fig. 4: Selective coating diffusion barrier after ageing analysis.

In this case, it is not possible to use barrier layers to avoid the self-migration of the silver. The solution taken for high temperature in HITECO project was the use of Molybdenum as mirror layer, since its refractory nature makes it less prone to migration problems.

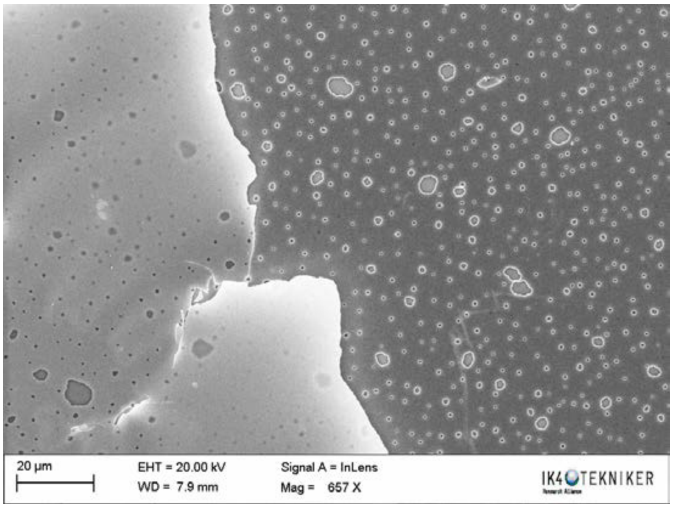

Fig 5: Silver IR mirror degraded after thermal test.

The change in the dielectric used for the Cermet in the HITECO absorber, imposed by the results of the ageing test, is an additional example of the detrimental effect that the combination of temperature and exposure time may have on the stability of the very thin optical layers that form a selective absorber. The original cermet developed for the HITECO absorber, developed in a small laboratory machine, was composed of a mixture of Molybdenum and Si_3N_4. When this coating was replicated in a larger scale coating machine for 4 meters long tubes, and applied on tubes at room temperature, it was observed that the resulting cermet lacked the required thermal stability. In the most extreme example, the cermet layer shown in Fig.6a (which was obtained form a GDOES analysis, as a small peak of Nitrogen between the Molybdenum and Silicon Oxide layers), almost completely disappeared after the thermal treatment for only 20 hours at 600ºC in high vacuum, as reflected in the Figure 6b. This strongly suggests that it will not reach the required durability under the working conditions required for the HITECO concept. Therefore, in the following developments the Si_3N_4 dielectric in the cermet had to be replaced by alumina, used for a long time in commercial plants working at 400ºC and showing a good thermal stability at 600ºC.

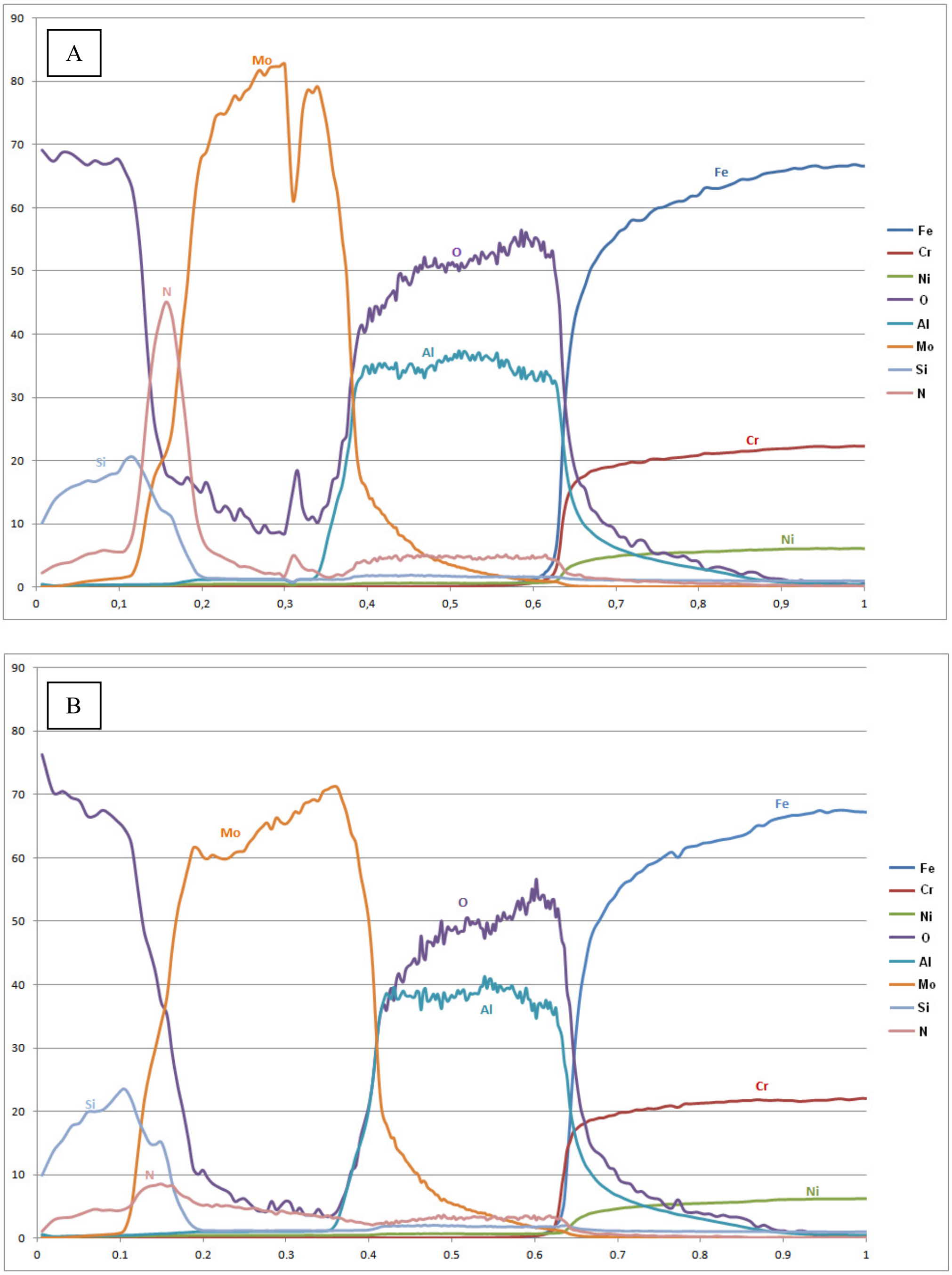

Fig. 6: GDOES of absorber stack with cermet based on Si_3N_4 (a) before and (b) after heat treatment.

3.2. Accelerated ageing and its consequences

From the discussion presented above stems the fact that it is crucial to characterize the state of the selective coating, as well as its evolution in time. In this context, the NECSO project [1] (which stands for Nanoscale Enhanced Characterization of SOlar selective coatings) is aimed at providing the end users with criteria and tools to guarantee that a selective coating will work properly during its expected operating life of around 25 years. To this end, characterization methods and standard protocols were established in order to guarantee the performance, durability and quality of the coating, both at medium and high temperatures. In addition to that, accelerated ageing protocols are proposed [5] to test the evolution in time of the various alternative coatings.

3.3. Impact of ageing on thermal losses

In order to evaluate the relevance of ageing and its impact on the overall performance of a CSP plant, a number of simulations using a computational model developed by us and capable of reproducing a wide range of operating conditions have been carried out. The model is based on subsequent energy balances carried out on the various surfaces of the receiver tube, assuming fully-developed and axisymmetric flow.

A parametric analysis where the temperature difference ΔT (defined as the heat transfer fluid temperature THTF minus the ambient temperature T∞) and the emittance of the absorber tube εabs were varied in the ranges 100 ≤ ΔT ≤ 600°C and 6 ≤ ε_{abs} ≤ 26% respectively has been performed. Note that the emittance is directly proportional to the temperature of the absorber tube, and is usually represented by a second or third order polynomial, but in this case we accounted for all the possible combinations for illustrative purposes. Fig. 11 shows the thermal losses in W/m of a receiver tube installed in a collector similar to the one described by Moss and Brosseau [7], with an assumed absorbance of 95%. For simplicity, we assumed a constant DNI of 950 W/m^2 and a uniform temperature of still air equal to 10°C in all the cases considered here. These results show, as expected, that heat losses significantly increased both with operating temperature and with the emittance of the selective coating. Although in all the temperature cases heat losses increased by a factor of roughly 3 when comparing the simulations at the highest emittance with the ones performed at the lowest, the slope of the increase becomes much steeper in the higher temperature range, and therefore it is important to properly characterize the optical properties of the selective coating at such conditions. In fact, at these temperatures the emittance will also be higher than at the lower temperature end, which further justifies additional efforts on this direction.

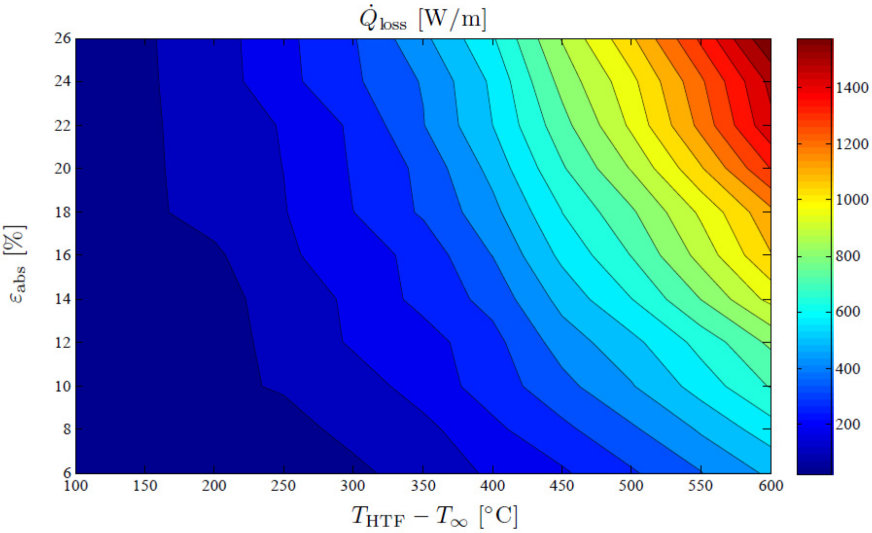

Fig. 7: Thermal losses in a CSP receiver as a function of temperature difference and emittance of the absorber tube.

This also shows the importance of NECSO [1], since Fig. 7 essentially shows that it is necessary to develop quality assurance criteria for selective coatings in order to bring the CSP technology to the high temperature regime of operation. Another crucial factor is the evolution of the optical properties in a selective coating after several years of operation. Higher temperatures imply that a subtle increase in the absorber tube emittance may lead to significantly lower performance, and that is why several accelerated ageing protocols are currently under development: they will help improve the design of selective coatings, and predict the extrapolated performance in time. To illustrate this effect, it has been simulated the ageing process of two selective coating samples, at 100, 400 and 600°C, at three reference operational stages: (1)initial stage no degraded, (2) low degraded by operation and (3) highly degraded. Please note that these values are dependant of the kind of coating, the operative conditions in each solar plant and the working time in which the coating has been exposed to these conditions.

The increase in emittance values as the three operational stages are progressively reached is shown in Fig. 8 (top), where an absorbance of 95% is considered for stage 1 (initial), and a reduced value of 90% is assumed in stages 2 and 3 (degraded and highly degraded respectively). It means an impact not only in thermal losses but a reduction in energy gain. This simplified model is used to show the effect of ageing, and more importantly the differences found at medium and high temperature ranges of operation. Note that in the highly degraded state emittance rise from 9% to 16% at ΔT=400°C and from 12% to 22% at ΔT=600°C (a factor of around 1.8 in both cases).

Given these emittance trends, it has been performed simulations using the same model and standard operating conditions as in Fig. 7 to determine the increase in heat losses for the two conditions. These results are shown in Fig. 8 (bottom), with the following results: heat losses increased from 267 to 435 W/m at medium temperature, and from 817 to 1465 W/m at high temperature. Note that this yields an increase by a factor of 1.63 and 1.8 at medium and high temperatures respectively, which again shows the critical effects of ageing at higher temperatures. It is also relevant to note that although similar trends are observed at lower temperatures of ΔT=100°C, heat losses are significantly lower than the ones encountered on the common operation regimes.

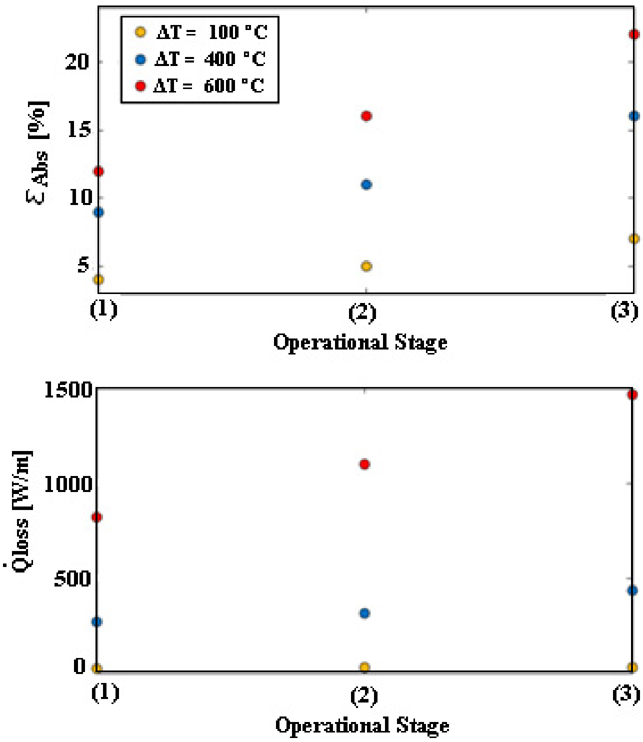

Fig. 8: (top) simulated evolution of Emittance in a selective coating at 100, 400 and 600°C, together with (bottom) computed heat losses.

3.4. Impact of ageing on the energy gain

As it was described in the figure 6, the degradation can affect the cermet changing the absortance (A) by the oxidation of the layers. It has been considered in current analysis only two operative situations a) no degraded coating with an absortance of around 95% and b) degrades coating with an absortance of 90%. Please note, as it was previously pointed out, that this effect is additional to the increase of thermal losses by increase of emittance, being both factors involved in a higher energy cost.

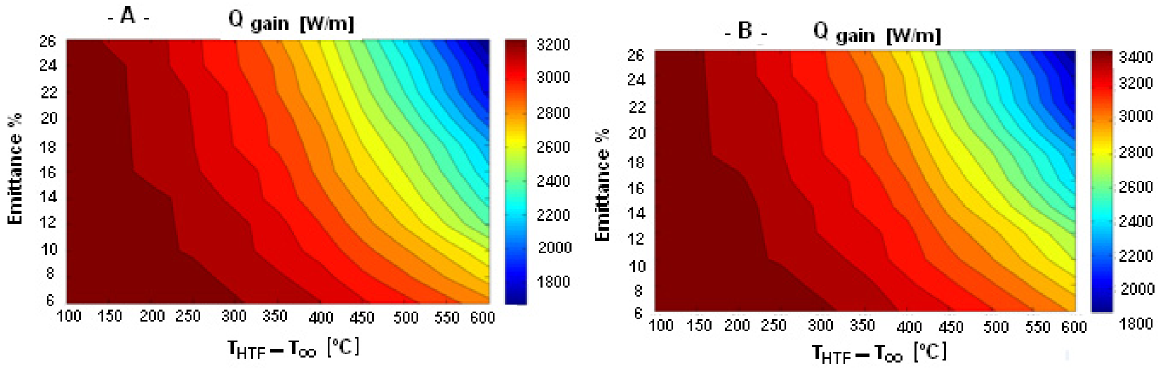

Fig. 9: Simulation of energy gain using a coating with A=90% (A) and A=95% (B)

According the simulated analysis, the net gain, for medium temperature case (400ºC), the evolution is from an initial stage with emittance of 9% and absortance of 95% (net gain 3200 W/m) to a degraded stage with an emittance of 16% and absortance 90% (net gain of 2800 W/m).

For high temperature (600ºC) the trend is ever more evident so, the evolution is from an initial stage with an emittance 12% and absortance 95% (net gain of 2700 W/m) to a degraded stage with emittance 22% and absortance 90% (net gain of 1900 W/m). Please, take into account that the exergy performance is much greater at high temperatures and that the parabola considered in both cases has the same aperture area.

These results are explicit enough to emphasize the importance of monitoring the optical values in the solar coatings to reduce the cost of the energy produced.

4. Conclusions

In this study it has been shown that selective coating degradation during operation arises from instabilities on each layer, being this effect directly influenced by the operating conditions. This implies that an adequate Operation & Maintenance strategy will increase the expected life of the coatings. In addition to this, not only a stable selective coating is important, but it is also essential to quantify thermal losses, and extrapolate them in order to propose a strategy for the predictive maintenance. This is one of the challenges in the current state of the technology.

An adequate selective coating with stable optical conditions in time during its lifespan is crucial in CSP applications, especially at high temperatures. The computations described here show that, for medium temperatures (ΔT = 400°C), an increase in emittance from 9% to 16% increases heat losses from 267 to 435 W/m. At high temperatures (ΔT = 600°C), an increased emittance from 12% to 22% produces a rise in heat losses from 817 to 1465 W/m.

Innovative concepts of absorber tube using new selective coatings such as HITECO [4], together with protocols and criteria to define the ageing processes NECSO [1] will directly result in a reduction of electricity cost, thus making CSP plants economically competitive. This reduction arises from an increase in efficiency, more reliable solar plants and from a reduction in the CAPEX and OPEX (according to a design-to-cost strategy).

Acknowledgements

The research leading to these results is founded from the European Union 7th Framework Programme (FP7/2007-2013) under grant agreements n° 256830 and nº 310344 (HITECO and NECSO projects).

References

[1] Barriga J, Ruiz-de-Gopegui U, Goikoetxea J, Coto B and Cachafeiro H; Selective coatings for new concepts of parabolic trough collectors, SolarPACES 2013, International Symposium on Concentrating Solar Power and Chemical Energy Systems, Las Vegas; 2013.
[2] Kennedy C.E, Review of Mid- to High-Temperature Solar Selective Absorber Materials; NREL/TP-520-31267; July 2002
[3] Cachafeiro H, New concepts advance thermoelectric energy; EuroPhotonics; Winter 2012; pags 26-28.
[4] Carrascosa Perez, M, García-Miján Gomez A, Luna Sánchez M and Rueda Jiménez F; Radiation heat collection device; Patent PCT/EP2010/057189. 2010. ARIES, ES.
[5] Mateu E, Sánchez M, Pérez D, Garcia de Jalón A, Forcada S and Heras C; Optical characterization test bench for parabolic trough receivers; SolarPACES 2011, International Symposium on Concentrating Solar Power and Chemical Energy Systems, Granada; 2011.
[6] Moss T.A, and Brosseau D.A.; Final Test Results for the Schott HCE on a LS-2 Collector; Report Sandia, SAND2005-4034, 2005.